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SUMMARY

The effect of moisture on the stability of thin-film cadmium sulfide cells was studied. The observed changes in the photovoltaic output and spectral response were indicative of performance loss. Cells made with Capran adhesive were degraded at rates directly proportional to the amount of moisture present. Cells in humidities near 100 percent suffered total loss of performance in a few days, whereas in humidities below 50 percent the loss was about 1 percent a day. In either case the mechanism appeared to be similar. Water permeated the plastic covering of the cell and was adsorbed in the junction region, and thus the number of traps which acted as recombination centers was increased. Less current was then collected by the grid and the performance consequently declined. The degradation of cells that lost less than 50 percent of their original performance was reversible and could be restored by heating in a vacuum for several hours. These cells had a loss in short-circuit current with little change in the diode characteristics. An irreversible degradation set in when the cells lost more than 50 percent power. These latter cells were distinguished by increased series resistance and a deterioration of the diode characteristics. To avoid moisture degradation, the hygroscopic Capran adhesive was replaced with epoxy resin to encapsulate cells with apparent success.

INTRODUCTION

As the result of research and development efforts cadmium sulfide thin-film solar cells have emerged as a potential space electric power source (ref. 1). This emergence into prominence resulted not only from the increased power outputs (refs. 2 and 3) but also from radiation studies that verified earlier predictions that these cells would be little affected by large doses of electrons and protons (ref. 4). Thermal cycling tests have shown that thin-film cells can be constructed to withstand thousands of cycles from

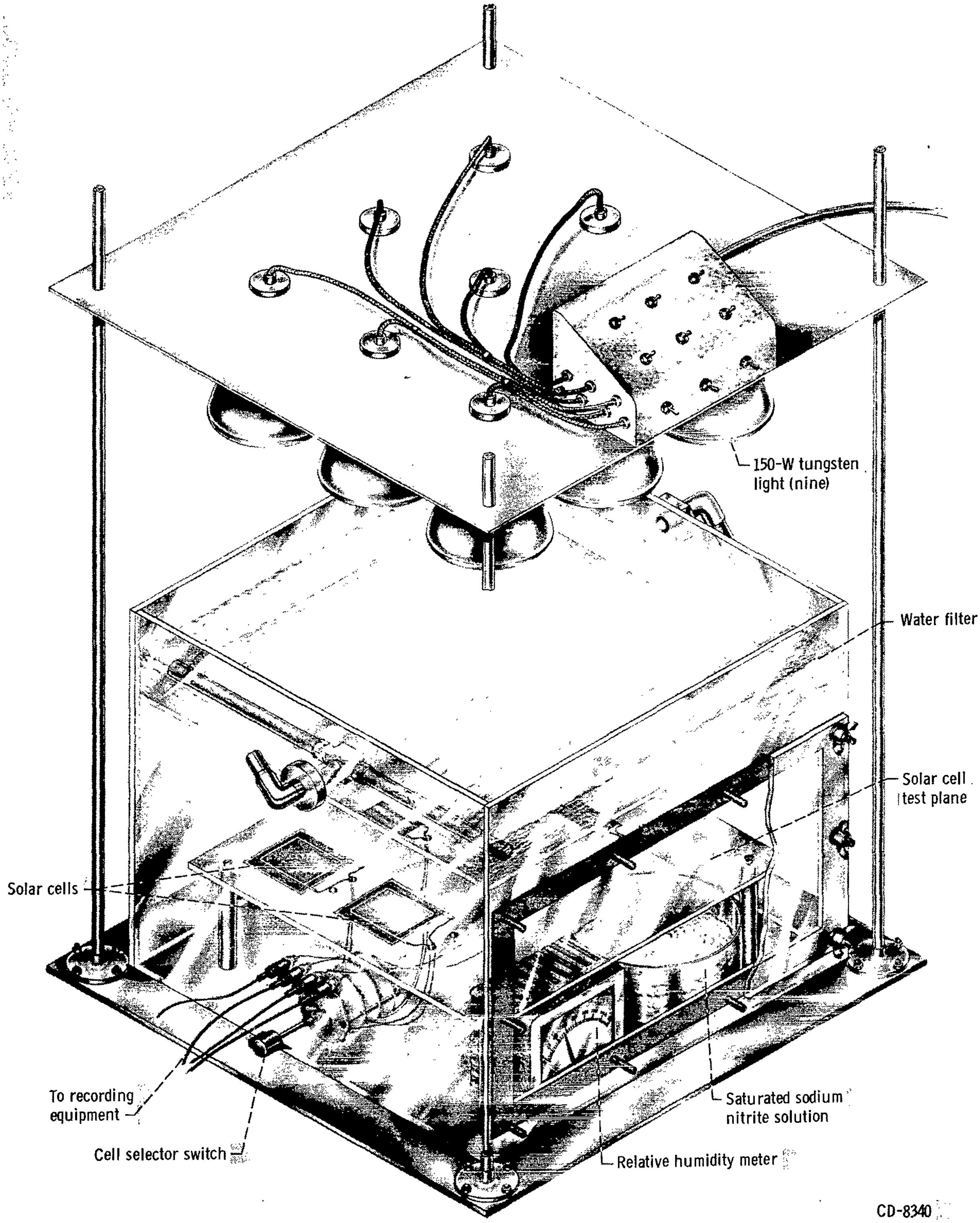


Figure 1. - Humidity chamber.

-100° to 60° C (173° to 333° K) without loss of power (ref. 5). When these results are included in the evaluation, the thin-film cadmium sulfide cells appear quite promising for use in space.

Statements have appeared from time to time in the literature on the stability of cadmium sulfide solar cells in moisture (refs. 1, 3, and 6). In general, the effects of moisture have been minimized, mainly on the assumption that the process is completely reversible.

The lack of corroborating data led to an examination of the moisture sensitivity of cadmium sulfide thin-film solar cells. Three types of cells were included in the study: (1) cells encapsulated in Mylar and Kapton with Capran adhesive, (2) cells encapsulated in Mylar and Kapton with an epoxy adhesive, and (3) cells without a protective plastic cover. The cells were placed in a humidity chamber at ambient temperature and pressure. Observable changes in the photovoltaic output and spectral response of the solar cells followed the process of degradation. Photovoltaic properties of interest (open-circuit voltage, short-circuit current, and maximum power) were measured directly from the current-voltage curves obtained under a standard light. Additional cell parameters (series resistance, shunt resistance, and junction properties) were calculated from the same curves. Another part of this work was the study of the power output recovery of the cell by exposure to heat and/or vacuum for extended periods of time. Vacuums as low as 10^{-7} torr (1.33×10^{-5} N/sq m) and temperatures up to 180° C (453° K) were used.

APPARATUS

Humidity Chamber

The humidity damage experiments were conducted in the chamber shown in figure 1. The chamber, including the door, was constructed from 0.25-inch (6.35×10^{-3} m) clear plastic; the door was sealed with a foam rubber gasket. The light source was composed of nine 150-watt tungsten floodlamps which could be controlled either together or separately. The light from the floodlamps was thermally filtered through a 2-inch (5.08×10^{-2} m) layer of water. Calibrated silicon solar cells used to monitor the intensity of the light ensured a constant light intensity at the test plane. Although it was not important to provide any prescribed intensity level, it was important to maintain a constant level so that relative changes in cell characteristics could be observed during the course of the tests. Saturated aqueous solutions of inorganic salts were used to maintain constant humidity inside the test chamber. As long as there was an excess of the solid phase and the temperature remained constant, the system provided constant humidity without any attention. Sodium nitrite was used at ambient temperature to maintain the 65-percent relative humidity used for most of the tests. A humidity meter was used to measure the relative humidity. The cells were soldered to output terminals on the side of the chamber to more easily obtain the current-voltage curves when the cells were left in the box during the run. In the tests conducted at 65-percent relative humidity the cells were removed from the humidity chamber so that their photovoltaic properties could be measured more accurately and the spectral response of the cells determined.

Photovoltaic Measurements

The light source for routine current-voltage measurements (fig. 2) was four 600-watt tungsten-iodine lamps operated at a color temperature of 3100° K. The light was filtered through 2 inches (5.08×10^{-2} m) of water. The lamps were aimed to give a uniform intensity over a 4-inch (10.16×10^{-2} m) square, with a uniformity better than 1 percent as checked by a 2-square-centimeter silicon solar cell. A constant temperature was maintained during the measurements by using a water-cooled base plate regulated to $25^{\circ}\pm1^{\circ}$ C ($298^{\circ}\pm1^{\circ}$ K). To ensure good heat transfer, the cells were held against the base plate with pressures from a vacuum "hold-down" not exceeding 6 pounds per square inch absolute. The intensity of the light was adjusted to 100 milliwatts per square centimeter by a primary standard cadmium sulfide cell (2 sq cm) calibrated as described in reference 7. Current-voltage curves were obtained with a four probe system and an electronic load with the output plotted on a X-Y recorder. Calibration of the system was checked periodically and was correct within 1 percent.

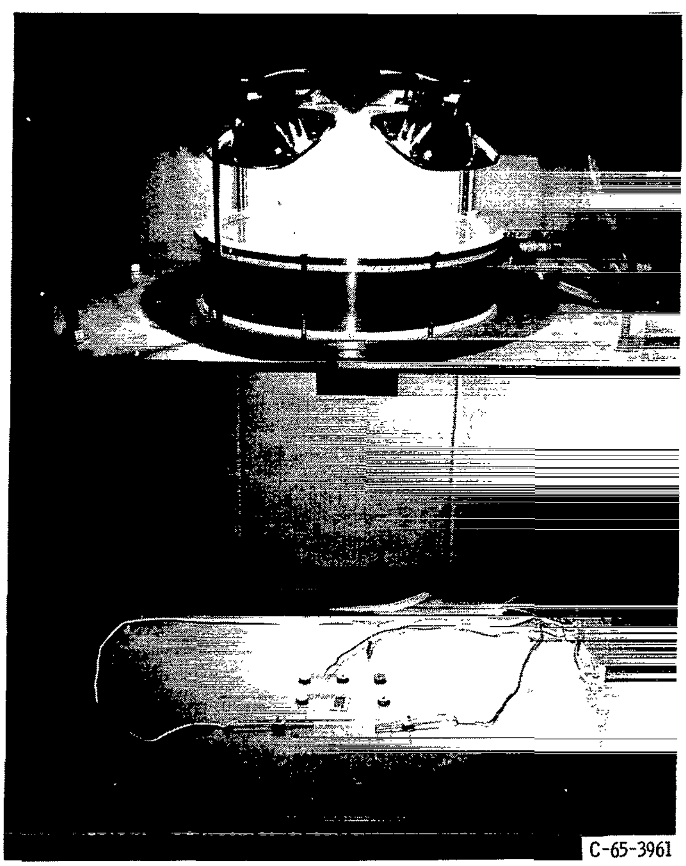


Figure 2. - Light source for current and voltage measurements.

Spectral responses of the cells were measured on the apparatus described in detail in reference 4. Eighteen monochromatic interference filters were used to cover the spectral range from 0.35 to 1.2 microns (0.35×10^{-6} to 1.2×10^{-6} m) in 0.05-micron (0.05×10^{-6} m) intervals. White-light bias was used for all measurements in this study. When the signal due to the white-light bias was balanced out, spectral responses as low as 1 microvolt could be measured.

Solar Cells

The cadmium sulfide solar cells used in these studies were similar in design to those currently being produced (refs. 2 and 3). Briefly, they consisted of a thin metal (copper or molybdenum) or plastic (Kapton) substrate (1 or 2 mils (2.54×10^{-5} or 5.08×10^{-5} m) thick) on which is deposited about 1 mil (2.54×10^{-5} m) of cadmium sulfide followed by a barrier layer of copper sulfide. The current-collecting metal grid can be attached to the cell by one of several methods. If a preformed grid, such as copper, gold, or silver, is used, it is cemented to the cell with conducting epoxy. If the grid is not cemented, a plastic cover holds it in contact with the cell. A second method is to electroplate the grid directly onto the cell. Regardless of the method used to apply the grid, a protective cover would be required for thermal control in space. Cadmium sulfide solar cells are usually encapsulated in Mylar or Kapton plastic with an adhesive. The cells made with Capran adhesive (cells 1 to 14, table I) did not have cemented grids, but depended on the Capran and plastic to hold the grids in contact with the barrier. The cells using epoxy adhesive to hold the plastic cover in place (cells 23 to 27, table I) also used a conducting epoxy to cement the grids to the cells. It was not necessary to use a plastic cover to hold the electroplated grids in place. Therefore, in this study, cells 15 to 22 (table I) were left uncovered.

The standard size solar cell was approximately 3 by 3 inches (7.62×10^{-2} by 7.62×10^{-2} m) in area and about 5 mils (1.27×10^{-4} m) thick. Some of the cells, however, were 1 by 2 centimeters in area. The cells were very flexible and weighed between 2 and 3.5 grams per 50 square centimeters of area.

PROCEDURE

Before any humidity tests were started, the solar cells were characterized as completely as possible under standardized conditions. The current-voltage curve at several light levels, forward and reverse diode characteristics, and the spectral response were usually measured. The cells were mounted in the test chamber, and the chamber was sealed. The chamber had been previously conditioned at the relative humidity used for the test. If the cells were left in the chamber during the run, current-voltage curves

TABLE I. - DEGRADATION AND RECOVERY OF CADMIUM SULFIDE SOLAR CELLS

Cell	Cell area, sq cm	Encapsulant	Efficiency, percent	Relative humidity, percent	Percent of original after degradation			Percent of original after recovery					
					Open-circuit voltage	Short-circuit current	Maximum power	Open-circuit voltage	Short-circuit current	Maximum power	Open-circuit voltage	Short-circuit current	Maximum power
								In vacuum of 10^{-7} torr (1.33×10^{-5} N/sq m) for 7 days			In vacuum of 10^{-3} torr (1.33×10^{-1} N/sq m) at 180° C (453° K) for 2 hr (7.2×10^{3} sec)		
1	45	Kapton	2.3	45	100	95	93	101	88	82	105	102	105
2		Mylar	2.9	85	98	88	90	100	98	95	97	106	103
3		Kapton	2.4	45	98	80	79	99	87	85	---	---	---
4			2.8	85	97	75	79	98	70	70	100	115	117
5			2.4	45	76	76	71	99	80	74	100	84	88
6			2.6	85	91	77	55	99	73	52	100	116	77
7			2.3	85	93	68	52	99	79	67	105	119	121
8		Mylar	3.1	85	89	35	36	92	45	44	94	61	70
9		Kapton	2.5	85	92	37	34	90	33	43	93	66	99
10		Kapton	2.6	85	88	34	26	96	58	46	101	115	111
11		Mylar	2.6	85	84	32	24	86	33	33	83	42	38
12		Kapton	2.6	85	85	24	18	87	24	20	---	---	---
13	1.5	Mylar	5.8	65	91	52	29	---	---	---	88	81	[a,b]32
14	1.5	Mylar	5.8	65	90	37	27	---	---	---	89	42	[c,b]36
15	2.5	Inorganic	3.0	75	99	80	69	99	83	[d]64	98	105	98
16	2.1		3.1	75	97	69	64	96	68	[d]63	102	101	111
17	2.6		3.3	75	98	68	61	95	65	[e]55	102	95	101
18	2.4		3.8	75	68	33	17	---	---	---	96	60	62
19	2.5		3.1	75	70	32	16	---	---	---	110	97	125
20	2.1		3.9	75	77	51	29	63	52	[e]14	96	81	62
21	2.1		1.7	75	49	21	6	---	---	---	92	43	41
22	2.1		2.0	75	21	20	2	---	---	---	81	32	21
[f]23	53	Mylar	4.2	66	101	98	98	---	---	---	---	---	---
[g]24	55	Mylar	4.5	66	101	96	98	---	---	---	---	---	---
[g]25	55	Mylar	4.6	66	100	99	94	---	---	---	---	---	---
[g]26	55	Mylar	3.6	66	101	98	97	---	---	---	---	---	---
[g]27	55	Mylar	3.2	66	102	98	98	---	---	---	---	---	---

[a]12 hr.
[b]Relamination did not change value.
[c]16 hr.
[d]3 Days.
[e]2 Days.
[f]109 Days in humidity chamber.
[g]43 Days in humidity chamber.

were made immediately. These values were used as the initial values for the cells; any degradation was noted by comparing subsequent cell parameters with those initially obtained. Where additional properties (e.g., spectral response) were desired, the cells were periodically removed from the chamber to obtain the data. The time the cells were outside the humidity chamber was kept to a minimum; as a result, little or no effect was attributed to their removal.

RESULTS AND DISCUSSION

It has long been observed that cadmium sulfide solar cells fabricated with Capran adhesive have been degraded by exposure to ordinary ambient conditions, but the number of variables involved obscured the critical parameters responsible for the results. The effect of several variables is shown in figure 3, where the percent degradation of the maximum power per day is plotted as a function of the relative humidity. The tests were conducted at ambient temperature, pressure, and light conditions. Cells encapsulated with Kapton were degraded faster than those encapsulated in Mylar, with the former cells having the higher vapor permeability rate. The cells tested at 74-percent relative humidity were made with electroplated grids and were coated with magnesium fluoride. For all practical purposes the cells were without a protective coating. Both optical and electron microscopy revealed that the coating only partially covered the surface and was completely covered with microcracks. In the presence of moisture the cells behaved like uncovered cells. It appears that the rate of degradation depends on the rate at which water can reach the surface of the cell. Although at high relative humidities the stable life of a cadmium sulfide solar cell is very short, the rate of degradation at low humidities is quite small and under certain conditions could even be tolerated.

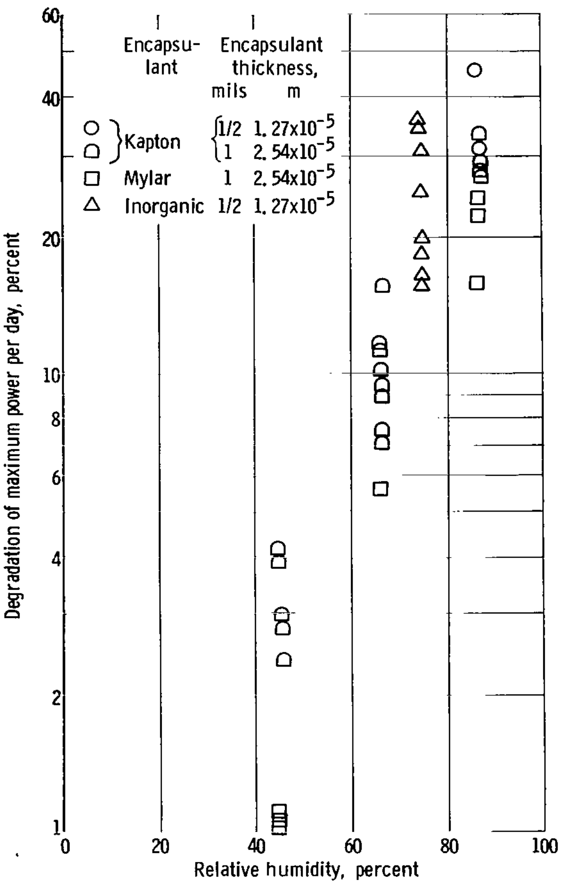


Figure 3. - Degradation rate of maximum power of thin-film cadmium sulfide solar cells.

The relation between the parameters examined and the current output of the solar cell is shown in the following equation (from ref. 8):

$$I = \mathcal{I}_0\left\{\exp\left[\frac{q}{AkT}(V - IR_s)\right] - 1\right\} - I_L + \frac{V}{R_{sh}} - \frac{IR_s}{R_{sh}} \tag{1}$$

where

I	current output
$\mathcal{I}_0$	diode reverse saturation current
q	electronic charge
A	constant
k	Boltzmann constant
T	absolute temperature
V	voltage output
R_s	series resistance
I_L	light-generated current
R_{sh}	shunt resistance

The current and voltage of the solar cell can be referred to as the photovoltaic output characteristics when the cell is illuminated. The cell is thus depicted as a current generator that is regulated by the diode properties of the junction materials. The diode reverse saturation current $\mathcal{I}_0$ and the constant A are determined by the material properties and will change only if the nature of the junction materials changes. The internal series

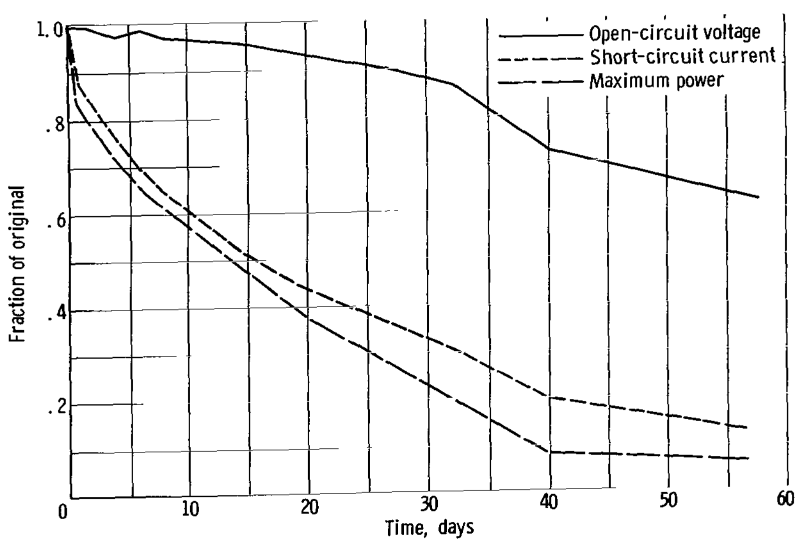


Figure 4. - Effect of moisture on short-circuit current, open-circuit voltage, and maximum power of cadmium sulfide solar cells.

resistance R_s and the shunt resistance R_{sh} represent direct losses of the generated current. Both must be carefully controlled to realize the maximum power output of the solar cell.

A detailed study of cell performance was made at 65-percent relative humidity. The cells had preformed gold grids and were encapsulated in either Kapton or Mylar with Capran adhesive. In figure 4 the average decrease in the performance of three cells is plotted as a function of exposure time in the humidity chamber. For the first month the open-circuit voltage V_{oc} decreased only slowly, while both the short-circuit current I_{sc} and the maximum power P_m decreased rapidly.

Other cell parameters of interest can easily be calculated by the method of Wolf and Rauschenbach (ref. 8) from the current-voltage data obtained at several different intensities of illumination. The series resistance was calculated at an arbitrarily chosen point close to the maximum power point on the current-voltage curve. In figure 5 the series

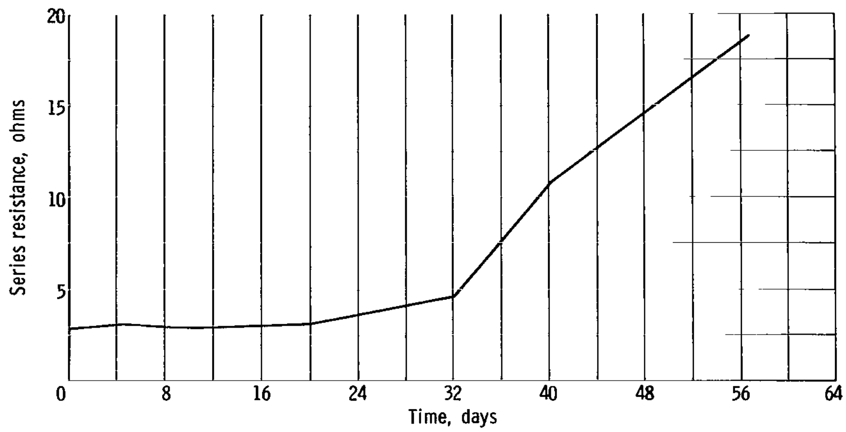


Figure 5. - Effect of moisture on series resistance of cadmium sulfide solar cells.

resistance R_s is plotted as a function of time. During the first month R_s changes very little; after that time R_s increases rapidly. The effect of moisture on the shunt resistance is shown in figure 6. The dark and light shunt resistances were determined from the slope of the current-voltage curve in the reverse direction, that is, where the voltage becomes negative at the I_{sc} condition. The light shunt resistance was measured using the standard 100-milliwatt per square centimeter light intensity. The lower light shunt resistance results from the high photoconductivity of cadmium sulfide. The effects of moisture on two junction parameters, A and $\mathscr{I}_0$, were followed by calculating their values according to reference 8. In figure 7, A and the saturation current are plotted against time. Both parameters changed very little for the first month; thereafter both increased rapidly.

Plotted in figure 8 are the relative spectral responses of two cells made with Capran adhesive, one cell encapsulated in Mylar and the other in Kapton, as they were degraded

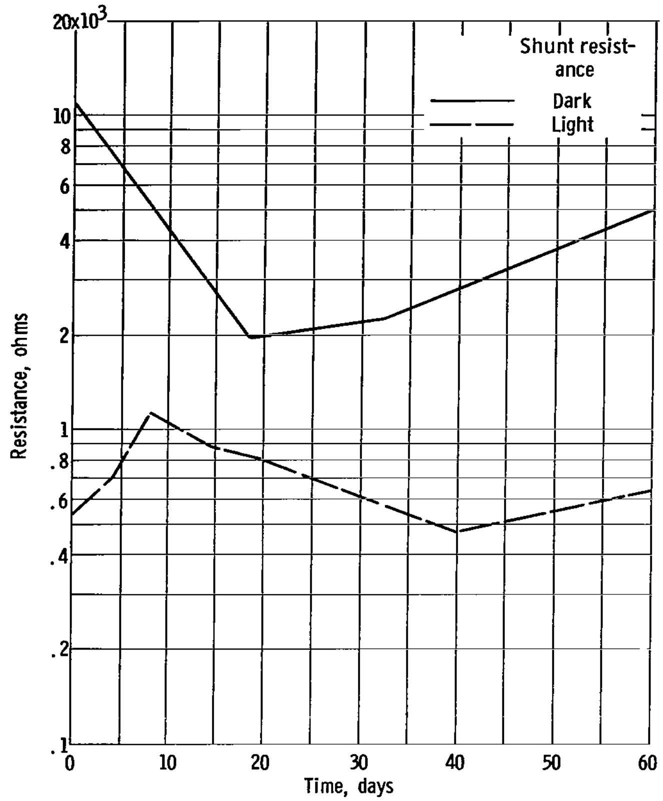


Figure 6. - Effect of moisture on shunt resistance of cadmium sulfide solar cells.

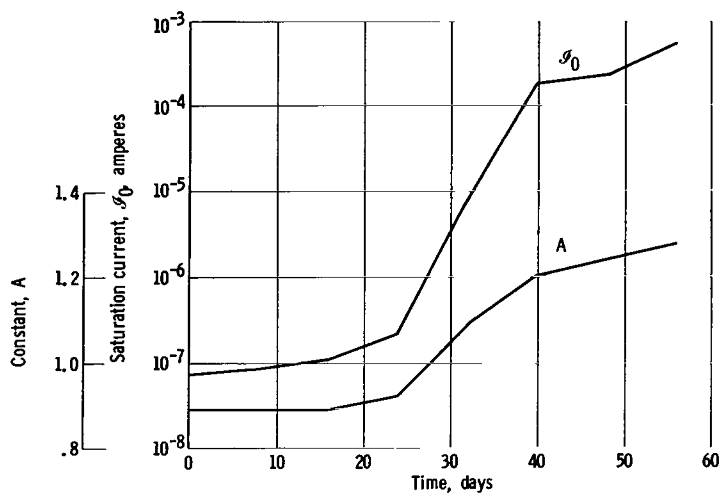
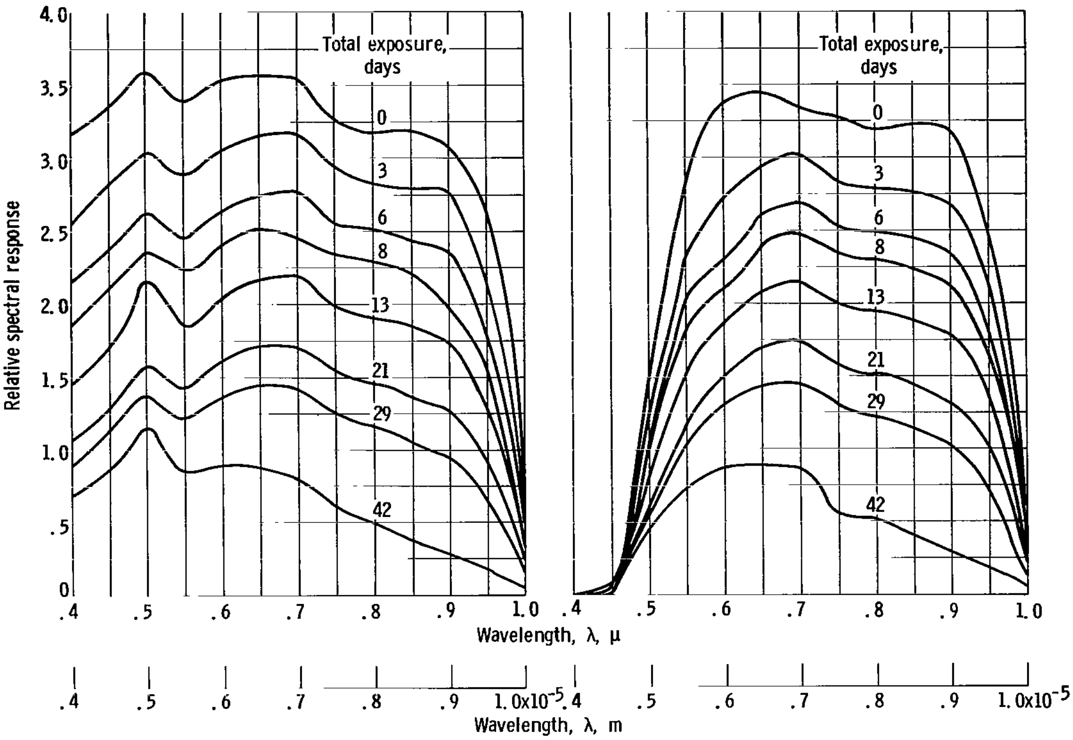


Figure 7. - Effect of moisture on diode reverse saturation current and constant A.



(a) Cell encapsulated in Mylar. (b) Cell encapsulated in Kapton.

Figure 8. - Effect of moisture on spectral response of cadmium sulfide solar cells made with Capran adhesive.

by 65-percent relative humidity. For wavelengths from 0.4 to 1.1 microns (0.4×10^{-6} to 1.1×10^{-6} m) the response decreased uniformly during the first month. Later the intensities were too low for accurate measurements, although there is an indication that the near-infrared response may have been affected more than the near-ultraviolet response. The data were taken with white-light bias.

It appeared from these data that water vapor penetrated the plastic cover of the cell, was absorbed either in the junction or on the barrier surface, and thus increased the number of traps which acted as recombination centers. Consequently, the current actually collected by the grid was reduced. At the same time the recombination centers probably played a prominent role in the dark shunt resistance, which was evidenced by the lower V_{OC}. It thus appeared that no damage was done to the junction, at least initially.

The attempts to remove adsorbed water from the cells and to recover the lost power met with only moderate success. Two experimental approaches to remove the water were investigated. In the first tests degraded cells were placed in a vacuum of 10^{-7} torr (1.33×10^{-5} N/sq m) at ambient temperature. They were removed periodically for testing. The results are shown in table I (p. 6). The greatest change in the output of the cells occurred at the beginning of the recovery test. Then the recovery rate decreased to zero and further pumping had no effect. If the vacuum improved the degraded cells at all, it did so very slowly.

The second step taken to rejuvenate the cells included both heat and vacuum. The cells were heated in a vacuum oven at various temperatures and periodically removed for testing. The results obtained at 180° C (453° K) are shown in table I (p. 6). Tests made at lower temperatures showed either no signs of improvement or produced rates of recovery much lower than those obtained at 180° C (453° K). All the cells leveled off at the values shown except cells 13 and 14, which passed through maximums. Of all the cells that had not been degraded below 50 percent of their original values, most recovered to their original levels; the remainder recovered a substantial portion of their lost power. Of the cells that had been degraded more than 50 percent, most recovered only a portion of their lost current and voltage. Thus, it appeared that the chances of complete recovery decreased as the amount of degradation due to moisture increased.

From the data on the degradation and recovery of the thin-film cells made with Capran adhesive, there seem to be two kinds of degradation: reversible and irreversible. Reversible degradation is characterized by a loss of short-circuit current, with little change in the diode characteristics. Irreversible degradation occurs after a 50-percent loss of power and appears to be associated with increases in series resistance and deterioration in the diode characteristics. Shirland (ref. 9) has suggested that the degradation may result from the hygroscopic nature of the Capran adhesive, which swells with water absorption. The use of a nonhygroscopic adhesive would avoid this problem.

Solar cells have been made with conducting epoxy resin used to cement the grids in place and epoxy adhesive used to encapsulate the cells in Mylar (ref. 10). In tests conducted at 66-percent relative humidity these cells have been very stable (cells 23 to 27, table I, p. 6). Cell 23 was exposed for 109 days, and the other four for 43 days. The relative spectral response of cell 23 is shown in figure 9. The response of this cell is quite different from those shown in figure 8; the main difference is the lack of near-ultraviolet response in cell 23. Part of this loss can be attributed to the transmission characteristics of the epoxy adhesive.

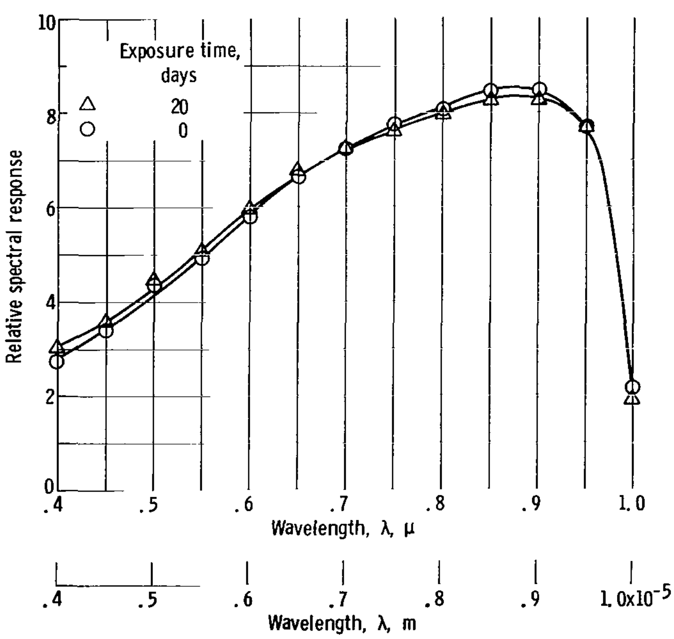


Figure 9. - Effect of moisture on spectral response of cadmium sulfide solar cell made with epoxy adhesive.

SUMMARY OF RESULTS

Thin-film cadmium sulfide solar cells encapsulated in plastic with Capran adhesive were degraded by exposure to water vapor. The extent of the degradation was directly related to the relative humidity of the environment. When cells were in near-100-percent humidity the total degradation of performance occurred in a few days, whereas in humidities below 50 percent the loss was only a few percent a day. Whether the degradation was rapid or slow, the mechanisms appeared to be similar. Water permeated the covering of the cell, was adsorbed in the junction region, and thus increased the number of traps which acted as recombination centers. Less current was then collected by the grid and the performance consequently declined.

The degraded performance of the cells was recovered by heating the cells at 180° C (453° K) in a vacuum, whereas vacuum without heat had little or no effect on the degraded cells. In this study only those solar cells that had been degraded less than 50 percent recovered all their lost power. The cells that had been degraded more than 50 percent recovered only a portion of the lost power. The degradation appears to be of two kinds: reversible and irreversible. The reversible degradation was accompanied by a loss of short-circuit current with little change in the diode characteristics. The irreversible degradation, which occurs after the cell loses more than 50 percent of its power, was associated with increased series resistance and a deterioration of the diode characteristics.

To avoid moisture degradation, the hygroscopic Capran adhesive has been replaced by an epoxy adhesive encapsulation of the thin-film cells. In the present tests these cells were insensitive to moisture during an extended period of exposure. The use of epoxy adhesive seems successful, but the reason for this moisture resistance is uncertain.

Lewis Research Center,
National Aeronautics and Space Administration,
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